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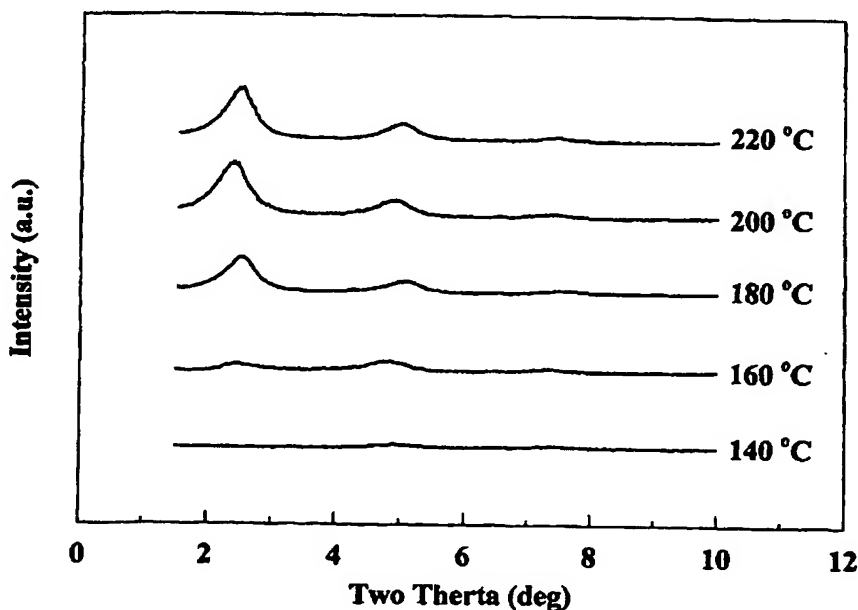
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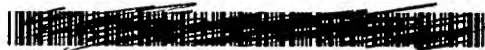
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(54) Title: PREPARATION OF CLAY-DISPERSED POLYMER NANOCOMPOSITE



(57) Abstract: Disclosed is a method for preparing a clay-dispersed polymer nanocomposite. In this method, a polymer, which carries oxygen atoms within the repeating units of its backbone and is thermodynamically compatible with a binder resin, is used as a matrix resin. Useful is poly(ϵ -caprolactone) owing to its thermodynamic compatibility with poly(styrene-co-acrylonitrile) copolymers, poly(acrylonitrile-co-butadiene-co-styrene) copolymers, and poly(vinylchloride) resins. Poly(ϵ -caprolactone) resins aid the binder resins to penetrate into silicate layers so that the silicate of the organophilic clay was completely delaminated to silicate lamellas.



Published:

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Preparation of clay-dispersed polymer nanocomposite

5 TECHNICAL FIELD

 The present invention relates, in general, to a method for the preparation of a clay-dispersed polymer nanocomposite and, more particularly, to the use of an oxygen atom-carrying polymer with thermodynamical compatibility with a binder resin in preparing a clay-dispersed polymer nanocomposite, thus delaminating clay completely to silicate lamellas.

PRIOR ART

 With the aim of overcoming limited physical properties of general-purpose plastics, the techniques for preparing clay-dispersed organic/inorganic composites are characterized in that clay ores of silicate layered structures are delaminated into silicate layers at nano levels and the silicate layers are dispersed in polymer resins, thereby upgrading general-purpose plastics to engineering plastics. Silicate layer, a structural unit of clay, is however difficult to disperse in polymer resins owing to its strong van der Waals attraction. To circumvent this problem, intercalants are suggested. According to a compounding technique, for example, an intercalant with a low molecular weight is introduced into the silicate layered structure to aid the penetration of polymer

resins into the structure, thereby delaminating clay
ores and dispersing the silicate layers in the resins.

However, the conventional compounding technique
has such a problem that, when nanocomposites are
5 prepared from some resins, including poly(styrene-co-
acrylonitrile)copolymer resins, poly(acrylonitrile-co-
butadiene-co-styrene) copolymer resins, and
poly(vinylchloride) resins, it is virtually impossible
to completely delaminate clay ores to the extent of a
10 silicate layer, which is a structural unit of clay. In
the nanocomposites of such resins, prepared by the
conventional compounding technique, in fact, there are
observed blocks of nano scales, which result from the
aggregation of several to tens silicate lamellas [see,
15 *Korea Polymer Journal*, 7, 310 (1999); *ibid*, 8, 95
(2000); *ibid*, 8, 120 (2000)]. The reason is that a
nitrogen and a chlorine atom, which are contained in the
repeating unit acrylonitrile of poly(styrene-co-
acrylonitrile) or poly(acrylonitrile-co-butadiene-co-
20 styrene) copolymer resins and the repeating unit vinyl
chloride of poly(vinylchloride) resin, respectively, is
smaller in electronegativity than is an oxygen atom,
which is present within organophilic clay, so that it is
not easy for the polymer chain to penetrate between
25 silicate layers.

DISCLOSURE OF THE INVENTION

Leading to the present invention, the intensive and thorough research on the preparation of clay-dispersed polymer nanocomposites, conducted by the present inventors, resulted in the finding that a polymer carrying oxygen atoms can itself penetrate into silicate structures and, when constituting a matrix for the composites, along with other polymers, help penetrate the binder resins into layered structure of silicates if they are thermodynamically compatible with the oxygen-carrying polymer.

Therefore, it is an object of the present invention to overcome the above problems encountered in prior arts and to provide a method for the preparation of clay-dispersed polymer nanocomposites, in which clay ores are completely delaminated to a silicate layer, which is a constituent minimum unit.

Based on the present invention, the object could be accomplished by a provision of a method for preparing a clay-dispersed polymer nanocomposite, which comprises introducing an oxygen-carrying polymer, alone or in combination with a thermodynamically compatible resin, as a matrix resin.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1a shows X-ray diffraction spectra of the nanocomposites of the present invention according to mixing periods of time.

Fig. 1b shows an X-ray spectrum of the clay-dispersed poly(styrene-co-acrylonitrile)copolymer nanocomposite according to the present invention, along with that of the clay-dispersed poly(ϵ -caprolactone) nanocomposite.

Fig. 2 shows X-ray diffraction spectra of the nanocomposites prepared at various temperatures according to the method of the present invention.

BEST MODES FOR CARRYING OUT THE INVENTION

The present invention pertains to a compounding technique of preparing a clay-dispersed polymer nanocomposite, in which a matrix resin, including a poly(styrene-co-acrylonitrile)copolymer, poly(acrylonitrile-co-butadiene-co-styrene) copolymer or poly(vinylchloride), is inserted into silicate structures with the aid of an intercalant, characterized in that a poly(ϵ -caprolactone) polymer is used.

Poly(ϵ -caprolactone) carries oxygen atoms within the repeating units of its backbone, as well as being thermodynamically compatible with poly(styrene-co-acrylonitrile) copolymer, poly(acrylonitrile-co-butadiene-co-styrene) copolymer and poly(vinylchloride).

Useful in the present invention is a poly(ϵ -caprolactone) resin ranging, in molecular weight, from 10,000 to 100,000.

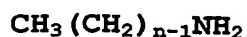
It is preferable that poly(ϵ -caprolactone) is used at an amount of 20-40 % by weight based on the total weight of the nanocomposite. For instance, if poly(ϵ -caprolactone) is added at an amount less than 20 % by weight, its compatibilization effect is too weak to bring about complete delamination into clay. On the other hand, more than 40 % by weight of poly(ϵ -caprolactone) may shield the expression of characteristic physical properties of other matrix resins.

In the present invention, clay to be dispersed in the matrix is treated with an intercalant in order to increase the dispersity of clay. The intercalant is preferably selected from the group consisting of hydroxyethylmethyloctadecylammonium chloride, which is represented by the following chemical formula 1; amines such as octyl amine, decyl amine, dodecyl amine, hexadecyl amine, and octadecyl amine, which are represented by the following chemical formula 2; and secondary amines represented by the following chemical formula 3:

Chemical Formula 1

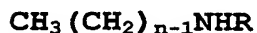


Chemical Formula 2



wherein n is 8, 10, 12, 16 or 18.

Chemical Formula 3



wherein n is an integer of 8-18 and R is a hydrocarbon.

As a constituent for clay, montmorillonite, which
5 swells in water, is preferably used.

Besides the polymer resins mentioned above, any
of the resins which are thermodynamically compatible
with poly(ϵ -caprolactone) can be used in the present
invention. chlorinated polyethylene is an example of
10 the thermodynamically compatible resins.

Preparation of clay-dispersed polymer
nanocomposites according to the present invention can
be achieved in either a one-pot or a two-pot manner.

As for the one-pot manner, it is conducted by
15 mixing a binder resin, poly(ϵ -caprolactone), and
organophilic clay and extruding them together. On the
other hand, according to the two-pot manner, poly(ϵ -
caprolactone) is mixed or extruded with an
organophilic clay to give a master batch, followed by
20 mixing with a binder resin for extrusion.

The following examples are set forth to illustrate
more clearly the principles and practice of this
invention to one skilled in the art. As such, they are
not intended to limit the invention, but are
25 illustrative of certain preferred embodiments.

EXAMPLE 1

Preparation of Poly(ϵ -caprolactone) Nanocomposite

An organophilic clay, such as that manufactured from Southern Clay Products Inc. U.S.A., identified as Closite 30A, was dry-blended at an amount of 5 % by weight with poly(ϵ -caprolactone) with a molecular weight of 80,000 at 100 °C at 120 rpm in a Minimax molder for various periods of time to obtain nanocomposites.

With reference to Fig. 1a, there are shown X-ray diffraction spectra of nanocomposites according to mixing periods of time. As seen in the spectra, the X-ray diffraction peak at around 2.5° disappears from the spectrum of the nanocomposite obtained when the mixing was continued for 20 min or longer; thus the silicate was completely delaminated with the aid of the intercalant in the nanocomposite.

EXAMPLE 2

Preparation of Clay-Dispersed Poly(styrene-co-acrylonitrile)copolymer Nanocomposite Using Clay-Dispersed Poly(ϵ -caprolactone) Nanocomposite

The clay-dispersed poly(ϵ -caprolactone) nanocomposite prepared in Example 1 was mixed at a weight ratio of 2:3 with a poly(styrene-co-acrylonitrile)copolymer resin, after which blending of the mixture was carried out at 100 °C for 5 min in a Minimax molder at 120 rpm to afford a clay-dispersed poly(styrene-co-acrylonitrile)copolymer nanocomposite.

With reference to Fig. 1b, an X-ray spectrum of this clay-dispersed poly(styrene-co-acrylonitrile)copolymer nanocomposite is shown, along with that of the clay-dispersed poly(ϵ -caprolactone) nanocomposite. In the X-ray spectrum of the nanocomposite of interest, an X-ray diffraction peak is detected at around 2.5° , but its intensity is very weak, indicating that organophilic clay is significantly dispersed.

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EXAMPLE 3

Preparation of Clay-Dispersed Poly(ϵ -caprolactone) Nanocomposite Through Twin-Screw Extruder and Preparation of Poly(acrylonitrile-co-butadiene-co-styrene) Copolymer Nanocomposite Using Master Batch Comprising the Same

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An organophilic clay, such as that manufactured by Southern Clay Products Inc., U.S.A., identified as Closite 30A, was dry-blended at an amount of 10 % by weight with poly(ϵ -caprolactone) with a molecular weight of 80,000 and the blend was extruded through a twin-screw extruder at 100°C at 250 rpm to give a nanocomposite in which the silicate of the organophilic clay was completely delaminated to silicate layers. After being pelletized, the clay-dispersed poly(ϵ -caprolactone) nanocomposite was blended at a weight ratio of 1:2 with a poly(acrylonitrile-co-butadiene-co-styrene) copolymer, followed by extruding the blend

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through a twin-screw extruder to produce a clay-dispersed poly(acrylonitrile-co-butadiene-co-styrene) copolymer nanocomposite.

EXAMPLE 4

5 One Pot-Type Preparation of Clay-Dispersed
Poly(styrene-co-acrylonitrile) Nanocomposite Through
Twin-Screw Extruder

With a matrix in which a poly(ϵ -caprolactone) with a molecular weight of 10,000 was contained at an
10 amount of 30 % by weight with the remaining portion being a poly(styrene-co-acrylonitrile) copolymer, Closite 30A, an organophilic clay commercially available from Southern Clay Products Inc., U.S.A., was dry-blended at an amount of 5 % by weight. At various
15 temperatures (220, 200, 180, 160 and 140 °C), the resulting blend was extruded through a twin-screw extruder at 250 rpm to produce nanocomposites.

Fig. 2 shows X-ray diffraction spectra of the nanocomposites prepared at various temperatures. As
20 apparent from these spectra data, the clay-dispersed organic/inorganic nanocomposite is made of completely delaminated silicate layers, which are constituent minimum units, when being extruded at 140 °C, but contained clay nanoblocks when being extruded at 220
25 °C.

EXAMPLE 5

Preparation of organophilic clay from Octadecylamine
and Preparation of Clay-Dispersed Poly(styrene-co-
acrylonitrile)copolymer Nanocomposite Using the Same

5 In a 3,000 ml beaker were charged 1,500 ml of
deionized water, 8.1 g of octadecylamine and 3.0 ml of
hydrochloric acid and the solution was heated to 80 °C
with stirring (Solution A). 1,500 ml of deionized
water and 30 g of clay, such as that manufactured by
10 Kunimine Co. Japan, identified as Kunifia F, were added
into another 3,000 ml beaker and heated to 80 °C. This
clay dispersion was poured to the Solution A and
stirred for 1 hour, after which a white precipitate was
separated by filtration. After being washed with
15 distilled water maintained at 80 °C, the precipitate
was dried to give 32.1 g of organophilic clay. This
was ball-milled to obtain a powder (C18-MONT) with a
size of 50 μm . Based on data of X-ray diffraction
tests, the space between silicate lamellas was
20 calculated to be 19 Å. The nanocomposite was measured
to comprise 74.0 % by weight of the content of pure
clay as measured by thermo gravimetric analysis. Taken
together, the X-ray diffraction data and the thermo
gravimetric analysis data demonstrate that the clay has
25 been transformed to organophilic clay.

To a polymer matrix in which poly(ϵ -caprolactone)
with a molecular weight of 10,000 was blended at an
amount of 30 % by weight with a poly(styrene-co-

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acrylonitrile)copolymer, the above organophilic clay (C18-MONT) was added at an amount of 5 % by weight and dry-blended. The resulting blend was extruded at 160 °C at 250 rpm to give a clay-dispersed poly(styrene-co-
5 acrylonitrile)copolymer nanocomposite in which the silicate of the organophilic clay was completely delaminated to silicate layers.

EXAMPLE 6

One Pot-Type Preparation of Clay-Dispersed
10 Poly(acrylonitrile-co-butadiene-co-styrene) Copolymer
Nanocomposite Using Twin-Screw Extruder

To a polymer matrix in which poly(ϵ -caprolactone) with a molecular weight of 10,000 was blended at an amount of 30 % by weight with a poly(acrylonitrile-co-
15 butadiene-co-styrene) copolymer, organophilic clay, such as that manufactured by Southern Clay Products Inc. U.S.A., identified as Closite® 30A, was added at an amount of 5 % by weight and dry-blended. The resulting blend was extruded at 160 °C at 250 rpm to
20 give a clay-dispersed poly(acrylonitrile-co-butadiene-co-styrene) copolymer nanocomposite in which the silicate of the organophilic clay was completely delaminated to silicate layers.

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EXAMPLE 7

**One Pot-Type Preparation of Clay-Dispersed
Poly(vinylchloride) Copolymer Nanocomposite Using
Single-Screw Extruder**

5 To a polymer matrix in which poly(ϵ -caprolactone)
with a molecular weight of 10,000 was blended at an
amount of 30 % by weight with a poly(vinylchloride)
polymer, organophilic clay, such as that manufactured
by Southern Clay Products Inc. U.S.A., identified as
10 Closite 30A, was added at an amount of 5 % by weight
and dry-blended. The resulting blend was extruded at
160 °C at 250 rpm through a single-screw extruder to
give a clay-dispersed poly(vinylchloride) polymer
nanocomposite in which the silicate of the organophilic
15 clay was completely delaminated to silicate layers.

INDUSTRIAL APPLICABILITY

Over the used polymers themselves, the clay-
dispersed polymer nanocomposites according to the
present invention were measured to be improved by 30-
20 50% in elastic modulus, by 5-10% in mechanical
properties, and by 50 °C in heat deflection
temperature. With these advantages, the nanocomposites
according to the present invention can replace
conventional ABS resin and various PVC resins for use
25 in housing electronic appliances.

The present invention has been described in an
illustrative manner, and it is to be understood that

the terminology used is intended to be in the nature of description rather than of limitation. Many modifications and variations of the present invention are possible in light of the above teachings.

5 Therefore, it is to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

CLAIMS

1. A method for the preparation of a clay-dispersed polymer nanocomposite, which comprises introducing poly(ϵ -caprolactone) , alone or in
5 combination with a thermodynamically compatible resin, as a matrix resin.

2. The method as set forth in claim 1, wherein the thermodynamically compatible resin is chlorinated polyethyleneor poly(vinyl chloride).

10 3. The method as set forth in claim 1, wherein the thermodynamically compatible resin is selected from the group consisting of a poly(styrene-co-acrylonitrile)copolymer, a poly(acrylonitrile-co-butadiene-co-styrene) copolymer, and a poly(vinyl
15 chloride).

4. The method as set forth in claim 3, wherein the poly(ϵ -caprolactone) ranges, in molecular weight, from 10,000 to 100,000.

5. The method as set forth in claim 1, wherein
20 the poly(ϵ -caprolactone) is mixed with a thermodynamically compatible resin, along with an intercalant, and extruded altogether, said thermodynamically compatible resin being selected from the group consisting of a poly(styrene-co-
25 acrylonitrile)copolymer, a poly(acrylonitrile-co-

butadiene-co-styrene) copolymer, and a poly(vinyl chloride).

6. The method as set forth in claim 1, wherein the poly(ϵ -caprolactone) is mixed with an organophilic clay and extruded or mixed to give a master batch, then, blended with a thermodynamically compatible resin, and extruded.

7. The method as set forth in claim 1, wherein the clay-dispersed polymer composite comprises clay which is intercalated by an intercalant.

8. The method as set forth in claim 7, wherein the intercalant is selected from the group consisting of hydroxyethylmethyloctadecylammonium chloride, represented by the following chemical formula 1;

Chemical Formula 1



Amines, represented by the following chemical formula 2;

Chemical Formula 2



wherein n is 8, 10, 12, 16 or 18.

secondary amines represented by the following chemical formula 3:

Chemical Formula 3



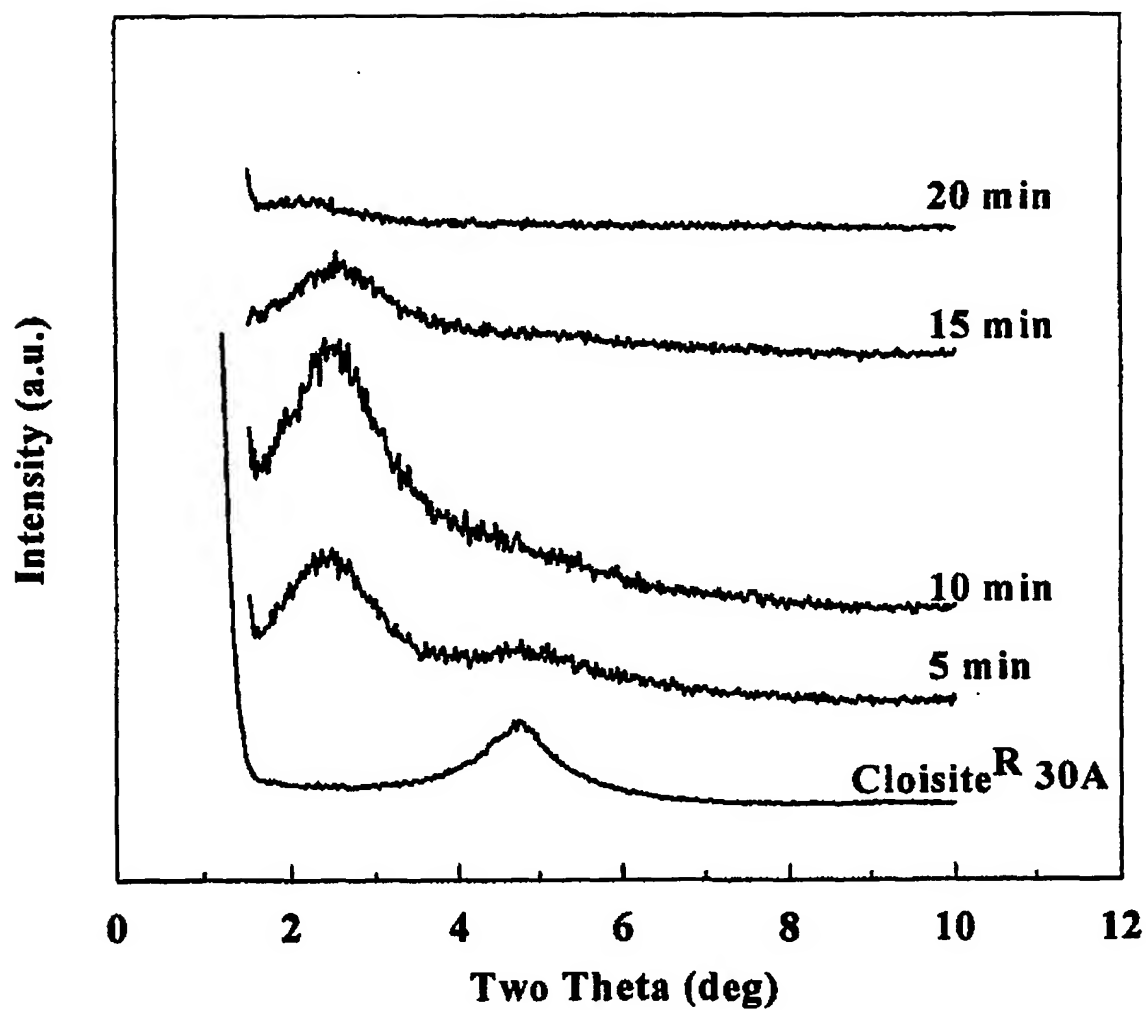
wherein n is an integer of 8-18 and R is a hydrocarbon.

9. The method as set forth in claim 1, wherein the clay-dispersed polymer composite comprises clay which contains montmorillonite.

10. The method as set forth in claim 1, wherein
5 the poly(ϵ -caprolactone) is used at an amount of 20-40 % by weight based on the total weight of the nanocomposite.

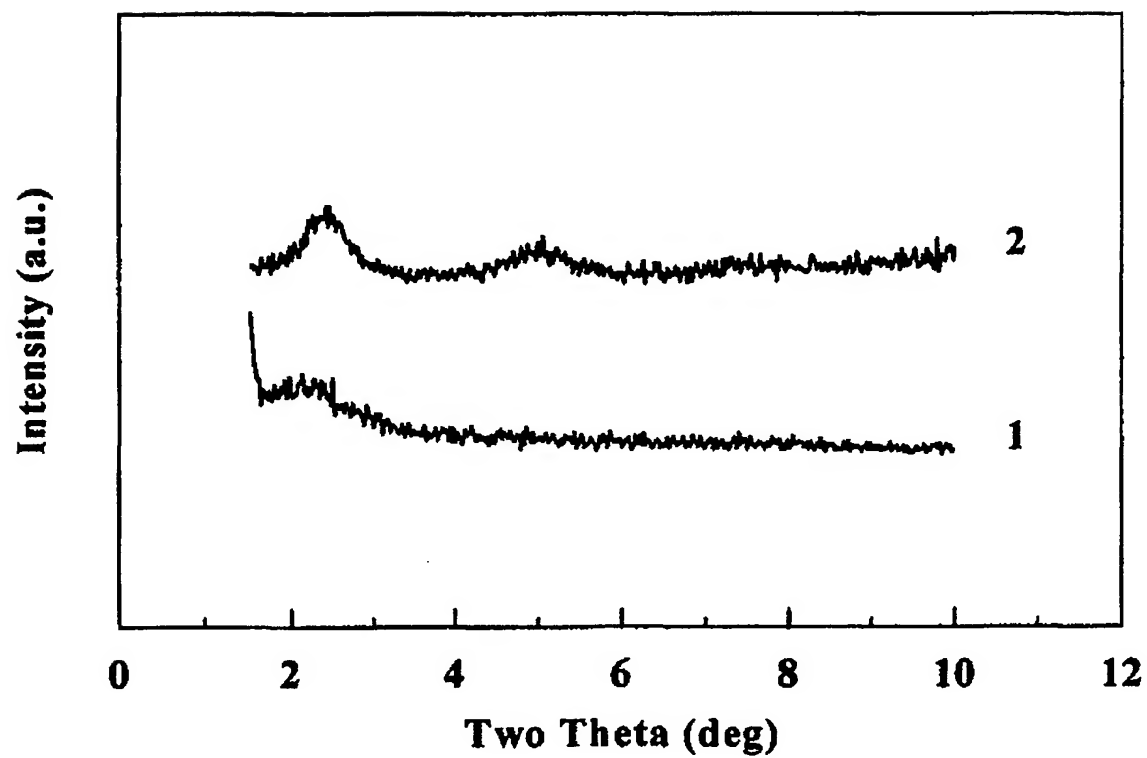
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FIG. 1a



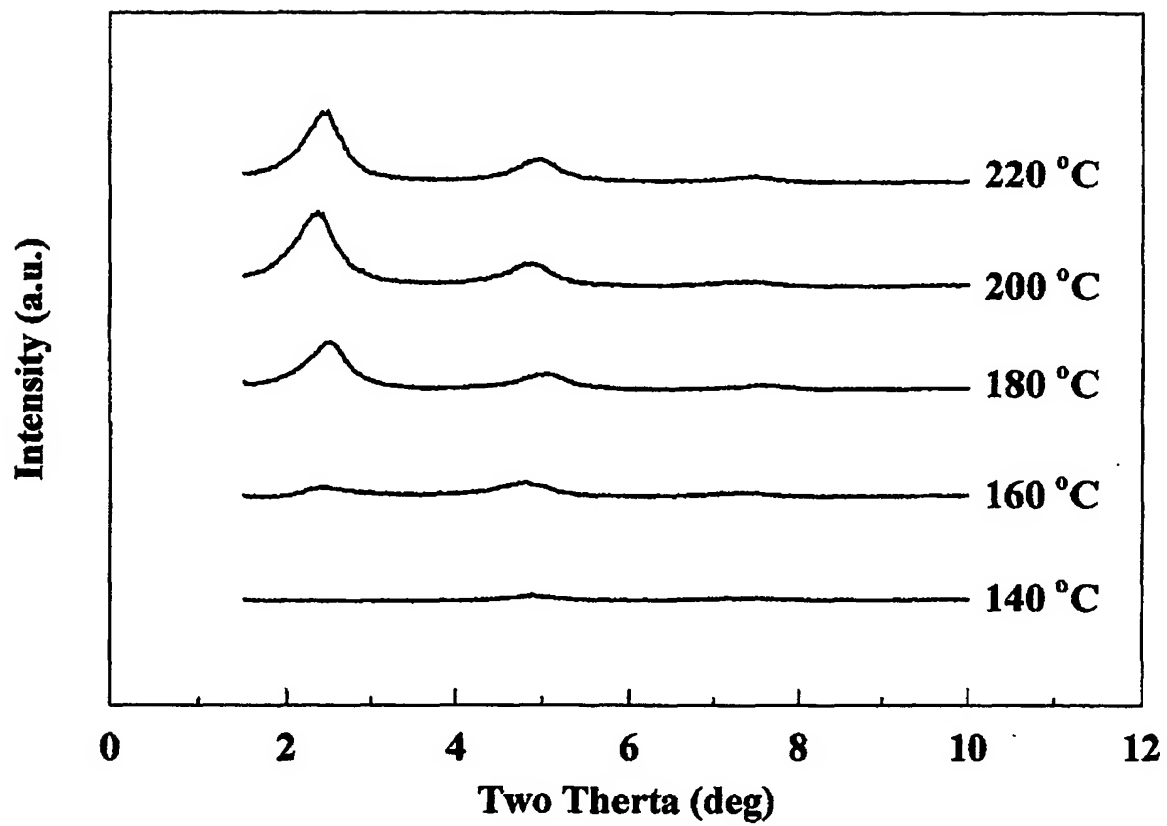
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FIG. 1b



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FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 00/01205

CLASSIFICATION OF SUBJECT MATTER

IPC⁷: C08J 3/20, 3/22, C08L 67/04, C08K 3/34, 9/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷: C08J, C08K, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, PAJ, WPI, SURFIP

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/34393 A1 (EASTMAN CHEMICAL COMPANY) 15 June 2000 (15.06.00) <i>claims 1,8,13-16,25,37,42, page 16, line 22 - page 17, line 6, page 21, line 22 - page 22, line 11, page 22, line 32 - page 23, line 2.</i>	1,6,8-10
X	WO 00/34380 A1 (EASTMAN CHEMICAL COMPANY) 15 June 2000 (15.06.00) <i>claims 1,10,15-18,31, page 18, lines 16-21.</i>	1,7-9
X	US 5830528 A (BEALL et al.) 3 November 1998 (03.11.98) <i>claims, column 19, line 24 - column 20, line 46.</i>	1,2,5,7,9
X	JP 01 197548 (DAICEL CHEM. IND. LTD.) 9 August 1989 (09.08.89) (abstract). [online] [retrieved on 2001-05-04]. Retrieved from: EPOQUE PAJ Database.	1,3-5

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

4 May 2001 (04.05.2001)

Date of mailing of the international search report

7 June 2001 (07.06.2001)

Name and mailing address of the ISA/AT

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 00/01205

Patent document cited in search report			Publication date	Patent family member(s)			Publication date
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				US	A	5804613	08-09-1998
WO	A	0034380				none	
WO	A	0034393				none	

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum)

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Box No. II	APPLICANT	
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Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)		Telephone No.
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<input type="checkbox"/> Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.		

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/KR 00/01205	International filing date (day/month/year) 24 October 2000 (24.10.2000)	(Earliest) Priority Date (day/month/year) 6 September 2000 (06.09.2000)
Applicant Korea Institute of Science and Technology et al.		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (See Box II).

4. With regard to the title,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:
Preparation of clay-dispersed polymer nanocomposite

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.: 2

☒ as suggested by the applicant.

☐ None of the figures.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
<i>If none of the following sub-boxes is used, this sheet should not be included in the request.</i>	
<p>Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p> <p>JUNG, Bum Suk</p> <p>Sataek-A 202, 39-1 Hawolgok-dong, Seongbuk-ku,</p> <p>Seoul 136-130, Republic of Korea</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>
State <i>(that is, country)</i> of nationality: KR	State <i>(that is, country)</i> of residence: KR
<p>This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p>Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p> <p>JO, Won Ho</p> <p>Geumho Town 306-1202, Yangjimaetul, Sunae-dong,</p> <p>Bundang-ku, Seongnam-si, Kyoungki-do 463-020,</p> <p>Republic of Korea</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>
State <i>(that is, country)</i> of nationality: KR	State <i>(that is, country)</i> of residence: KR
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<p>Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p> <p>KIM, Seong Woo</p> <p>Jugong Yeonrip 3-105, 811 Donam-dong, Cheju-si,</p> <p>Cheju-do 690-029, Republic of Korea</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>
State <i>(that is, country)</i> of nationality: KR	State <i>(that is, country)</i> of residence: KR
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State <i>(that is, country)</i> of nationality: KR	State <i>(that is, country)</i> of residence: KR
<p>This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p><input checked="" type="checkbox"/> Further applicants and/or (further) inventors are indicated on another continuation sheet.</p>	

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
<i>If none of the following sub-boxes is used, this sheet should not be included in the request.</i>	
<p>Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p> <p>KIM, Jun Kyung New Hyundai Apt. 102-204, 65 Hoigi-dong, Dongdaemun-ku, Seoul 130-050, Republic of Korea</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>
State (that is, country) of nationality: KR	State (that is, country) of residence: KR
<p>This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p>Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p> <p>LIM, Soon Ho Asia Seonsuchon Apt. 5-1205, 86 Jamsil-dong, Songpa-ku, Seoul 138-220, Republic of Korea</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>
State (that is, country) of nationality: KR	State (that is, country) of residence: KR
<p>This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p>Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p> <p>CHOE, Chul Rim Hosumaetul 404-101, 875 Janghang-dong, Ilsan-ku, Koyang-si, Kyoungki-do 411-380, Republic of Korea</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>
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<p>Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p> <p>PARK, Min Geugdong Apt. 102-204, SSangmun-dong, Dobong-ku, Seoul 132-030, Republic of Korea</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>
State (that is, country) of nationality: KR	State (that is, country) of residence: KR
<p>This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p><input type="checkbox"/> Further applicants and/or (further) inventors are indicated on another continuation sheet.</p>	

Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes: at least one must be marked):

Regional Patent

- ☐ **AP ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☐ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☐ **EP European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☐ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)


National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | |
|---|---|
| <input type="checkbox"/> AE United Arab Emirates | <input type="checkbox"/> LR Liberia |
| <input type="checkbox"/> AL Albania | <input type="checkbox"/> LS Lesotho |
| <input type="checkbox"/> AM Armenia | <input type="checkbox"/> LT Lithuania |
| <input type="checkbox"/> AT Austria | <input type="checkbox"/> LU Luxembourg |
| <input type="checkbox"/> AU Australia | <input type="checkbox"/> LV Latvia |
| <input type="checkbox"/> AZ Azerbaijan | <input type="checkbox"/> MA Morocco |
| <input type="checkbox"/> BA Bosnia and Herzegovina | <input type="checkbox"/> MD Republic of Moldova |
| <input type="checkbox"/> BB Barbados | <input type="checkbox"/> MG Madagascar |
| <input type="checkbox"/> BG Bulgaria | <input type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input type="checkbox"/> BR Brazil | <input type="checkbox"/> MN Mongolia |
| <input type="checkbox"/> BY Belarus | <input type="checkbox"/> MW Malawi |
| <input type="checkbox"/> CA Canada | <input type="checkbox"/> MX Mexico |
| <input type="checkbox"/> CH and LI Switzerland and Liechtenstein | <input type="checkbox"/> NO Norway |
| <input checked="" type="checkbox"/> CN China | <input type="checkbox"/> NZ New Zealand |
| <input type="checkbox"/> CR Costa Rica | <input type="checkbox"/> PL Poland |
| <input type="checkbox"/> CU Cuba | <input type="checkbox"/> PT Portugal |
| <input type="checkbox"/> CZ Czech Republic | <input type="checkbox"/> RO Romania |
| <input checked="" type="checkbox"/> DE Germany | <input type="checkbox"/> RU Russian Federation |
| <input type="checkbox"/> DK Denmark | <input type="checkbox"/> SD Sudan |
| <input type="checkbox"/> DM Dominica | <input type="checkbox"/> SE Sweden |
| <input type="checkbox"/> EE Estonia | <input type="checkbox"/> SG Singapore |
| <input type="checkbox"/> ES Spain | <input type="checkbox"/> SI Slovenia |
| <input type="checkbox"/> FI Finland | <input type="checkbox"/> SK Slovakia |
| <input checked="" type="checkbox"/> GB United Kingdom | <input type="checkbox"/> SL Sierra Leone |
| <input type="checkbox"/> GD Grenada | <input type="checkbox"/> TJ Tajikistan |
| <input type="checkbox"/> GE Georgia | <input type="checkbox"/> TM Turkmenistan |
| <input type="checkbox"/> GH Ghana | <input type="checkbox"/> TR Turkey |
| <input type="checkbox"/> GM Gambia | <input type="checkbox"/> TT Trinidad and Tobago |
| <input type="checkbox"/> HR Croatia | <input type="checkbox"/> TZ United Republic of Tanzania |
| <input type="checkbox"/> HU Hungary | <input type="checkbox"/> UA Ukraine |
| <input type="checkbox"/> ID Indonesia | <input type="checkbox"/> UG Uganda |
| <input type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> US United States of America |
| <input type="checkbox"/> IN India | <input type="checkbox"/> UZ Uzbekistan |
| <input type="checkbox"/> IS Iceland | <input type="checkbox"/> VN Viet Nam |
| <input checked="" type="checkbox"/> JP Japan | <input type="checkbox"/> YU Yugoslavia |
| <input type="checkbox"/> KE Kenya | <input type="checkbox"/> ZA South Africa |
| <input type="checkbox"/> KG Kyrgyzstan | <input type="checkbox"/> ZW Zimbabwe |
| <input type="checkbox"/> KP Democratic People's Republic of Korea | |
| <input type="checkbox"/> KR Republic of Korea | |
| <input type="checkbox"/> KZ Kazakhstan | |
| <input type="checkbox"/> LC Saint Lucia | |
| <input type="checkbox"/> LK Sri Lanka | |

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet:

- ☐
- ☐

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
item (1) 6 September 2000 (06.09.00)	2000-52689	KR		
item (2)				
item (3)				
<input type="checkbox"/> The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): _____				
<i>* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(iii)) See Supplemental Box.</i>				
Box No. VII INTERNATIONAL SEARCHING AUTHORITY				
Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):		Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority) Date (day/month/year) Number Country (or regional Office)		
ISA / AT				
Box No. VIII CHECK LIST: LANGUAGE OF FILING				
This international application contains the following number of sheets: request : 5 description (excluding sequence listing part) : 13 claims : 3 abstract : 1 drawings : 3 sequence listing part of description : _____ Total number of sheets : 25		This international application is accompanied by the item(s) marked below: 1. <input checked="" type="checkbox"/> fee calculation sheet 2. <input checked="" type="checkbox"/> separate signed power of attorney 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: 4. <input type="checkbox"/> statement explaining lack of signature 5. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s): 6. <input type="checkbox"/> translation of international application into (language): 7. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material 8. <input type="checkbox"/> nucleotide and/or amino acid sequence listing in computer readable form 9. <input type="checkbox"/> other (specify):		
Figure of the drawings which should accompany the abstract: 2		Language of filing of the international application: English		
Box No. IX SIGNATURE OF APPLICANT OR AGENT				
<i>Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).</i>				
 LEE, Jae Hwa				

For receiving Office use only	
1. Date of actual receipt of the purported international application:	2. Drawings: <input type="checkbox"/> received: <input type="checkbox"/> not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.

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